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The frequency of occurrence and discriminatory power of compounds found in human scent across a population determined by SPME-GC/MS

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Abstract

The composition of human scent collected from the hands is of interest to the medical community as a mechanism to diagnose disease and the forensic community as a means to investigate canine scent discriminations. An extensive survey of the volatile organic compounds (VOCs) identified in the headspace of hand odor samples utilizing solid phase micro-extraction gas chromatography/mass spectrometry (SPME-GC/MS) has been conducted to determine the constituents of the human base odor profile. Sixty-three compounds were extracted from the collected odor samples. The composition included acids, alcohols, aldehydes, hydrocarbons, esters, ketones and nitrogen-containing compounds. The majority of the compounds detected (79.4%) were present in less than one third of the individuals sampled. Spearman correlation coefficient comparisons at a match/no-match threshold of 0.9 produced a distinguish ability of 99.67% across the population.

Keywords: Human scent; Hand odor; VOCs; Canine; Human scent line-up

1. Introduction

The medical usefulness of volatile compounds produced by humans for the diagnosis of lung, breast, bladder, and skin cancer has been demonstrated through both instrumental [1–4] and biological analysis [5–7]. The value of compounds emanated by the body for diagnostic purposes relies upon a baseline determination of the presence and quantity of human odor compounds from an individual. The body odors of human individuals are determined by several factors, some odors are stable over time (genetically based) or they may vary with environmental or internal conditions. The authors have developed distinguishing terminology for these factors: the "primary odor" of an individual contains constituents that are stable over time regardless of diet or environmental factors; the "secondary odor" contains constituents which are also endogenous but are influenced by diet and environmental factors; and the "tertiary odor" contains constituents that are present due to exogenous sources (i.e., lotions, soaps, perfumes, etc.) [8].

The value of compounds emanated by individuals, collected as human scent evidence, are of importance to the law enforcement community. The Locard exchange principle proposes that a person cannot enter or leave an area or come in contact with an object, without an exchange of materials. In the case of scent evidence, the suspect leaves his scent in the location of the crime scene itself or on objects found therein. This form of trace evidence collected from a crime scene can be evaluated through the use of specially trained canines to determine an association between the evidence and a suspect.

The hypothesis that human scent is stable over time and distinguishable between individuals is the foundation on which canine identifications are based. Scientific research into the ability of canines to distinguish between individuals based on their scent supports this theory [9–12]. Thus far, there has been limited research as to the VOCs which comprise the human scent profile and their usefulness in distinguishing individuals by analytical methods [8,13–16]. To conduct such analysis, the frequency of

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occurrence of compounds extracted in human scent will require a larger population study to determine the variability of human-produced compounds among individuals.

Forensically, VOCs from the hand are of vast interest as it is the region of the body where known samples of human scent is most often collected by law enforcement for use by scent discrimination canines in comparison to collected samples from the crime. Hand odor is comprised of the secretions from eccrine and sebaceous glands plus odors from the microbial degradation of these secretions. Eccrine secretions are typically composed of 98% water, but also contain various organic and inorganic components [17]. Eccrine sweat originates in the extracellular fluid and therefore, reflects the chemistry of blood plasma [18]. The VOCs dissolved in blood include numerous alcohols, aldehydes, and alkanes [3]. Sebum from sebaceous glands consists of glycerides, free fatty acids, wax esters, squalene, and cholesterol. A wide variety of organic compounds can be found in the sebum, and may be influenced by diet and genetics [19]. It has been suggested that slight differences in the overall composition of the sebaceous fatty acid mixture may play a significant role in the unique individual odors in humans [19].

A significant portion of the scientific research into human odor has been conducted on secretions from the axillary (armpit) area [20,21] and the feet [22]. Identification of the compounds emanated by human hands that may influence mosquito host-seeking behavior have resulted in a listing of more than 300 compounds [23,24]. Many compound classes are present in human emanations including acids [8,14,15,20,21,24,25], alcohols [8,14,15,24–26], aldehydes [8,14,15,18,24–26], hydrocarbons [8,14,15,24,25,27], esters [14,15,24,25,28], and ketones [8,14,15,24,25,29]. The components of human secretions may not adequately represent the compounds, nor the abundances present in the headspace above this matrix. The headspace above skin on the forearm which comprises the odor has been directly sampled through solid phase micro-extraction gas chromatography/mass spectrometry (SPME-GC/MS) [29], and hand odor from a small subject population was also directly evaluated using an original sampling device and SPME-GC/MS [16].

The purpose of this paper is to conduct a large scale study of the volatile organic compounds (VOCs) present in the headspace of collected hand odors. The sampling method utilizes cotton gauze pads treated by supercritical fluid extractions (SFE) to remove the presence and possible interference of compounds in the background of the pads. Headspace SPME-GC/MS analysis of scent samples from the hands of 60 individuals (30 males and 30 females) provides a range of compounds extracted among individuals. This information can be used to assess the variation of these compounds across a population utilizing Spearman rank correlation coefficient comparisons, which has both diagnostic and forensic implications.

2. Materials and methods

2.1. Materials

Supercritical fluid extraction using methanol (HPLC grade, Fisher Scientific, Pittsburgh, PA) modified supercritical grade carbon dioxide (Air Products, Allentown, PA) was used as a pre-treatment for the gauze to create an "analytically clean" collection medium [14]. Gauze pads were DUKAL brand, 100% cotton, sterile, 2 × 2, 8ply, gauze sponges (DUKAL Corporation, Syosset, NY, USA). The vials used to hold the gauze were 10 ml glass, clear, screw top vials with PTFE/Silicone septa (SUPELCO, Bellefonte, PA, USA). All subjects used the same soap to wash the hands and forearms (Natural, Clear Olive Oil Soap, Life of the Party, North Brunswick, NJ, USA).

2.2. Pre-treatment of gauze pads by supercritical fluid extraction

An ISCO Model 260D Syringe Pump with an SFX 2-10 supercritical fluid extractor was used to perform the pre-treatment. Each supercritical fluid extraction began by filling the plastic extraction vessel with two pieces of sterile gauze pads. The optimum SFE conditions developed to extract organic volatile compounds from sterile absorbers were determined to be a 30 min static extraction time followed by a 10 min dynamic extraction time at an extraction temperature of 130 °C, pressure of 4500 psi, and a spike of 500 μl HPLC grade methanol directly into the extraction vessel. These samples were analyzed by identical SPME-GC–MS parameters for qualitative and quantitative analysis of the scent samples as described later in the text.

2.3. Method for hand odor sampling

A total of 60 subjects were evaluated, comprised of 30 males and 30 females ranging in age from 17–28 years old. The sampling protocol consisted of 30 s washing of the hands and forearms with olive oil based soap, a 2 min rinse of the areas with cool water, 2 min air drying, and 5 min of rubbing the palms of the hands over the forearms. A pre-treated 2 × 2 sterile gauze pad was removed from the 10 ml glass vial using tweezers rinsed previously with a 10% bleach solution. The gauze was placed in the palms of the subject's hands. The subjects sampled themselves by holding the pre-treated gauze between the palms of their hands as they walked outdoors for 10 min. At the end of that period, the gauze was re-sealed in the 10 ml glass vial. All samples were stored sealed in the 10 ml vials at ambient room temperature, and aged approximately 24 h prior to extraction. These storage conditions were chosen to simulate the conditions under which odor is collected for canine evaluation purposes, and no attempt was made to control microbial interactions with the substrate as it may make contributions to the overall odor profile. Samples were collected at an average temperature of 26.6 °C and an average humidity of 76%. Prior to the population sampling, the protocol was preliminarily tested five times each with a single male and a single female volunteer. These 10 samples were used to optimize the extraction time necessary when using the SPME fibers.

2.4. Determination of optimal SPME extraction time

Five samples each were collected from Male 1 and Female 1 on the same day following the previously described sampling